



Metallic lead recovery from lead-acid battery paste by urea acetate dissolution and cementation on iron

M. Volpe^{a,*}, D. Oliveri^b, G. Ferrara^a, M. Salvaggio^b, S. Piazza^a, S. Italiano^b, C. Sunseri^a

^a Dipartimento di Ingegneria Chimica dei Processi e dei Materiali, Università di Palermo, viale delle Scienze 90128, Palermo, Italy

^b Ecological Scrap Industry S.p.A. area industriale di Giammoro 98042, Pace del Mela, Messina, Italy

ARTICLE INFO

Article history:

Received 23 June 2008

Received in revised form 8 September 2008

Accepted 11 September 2008

Available online 24 September 2008

Keywords:

Lead recovery

Lead acid battery paste

Urea acetate

Iron reductants

Cementation

ABSTRACT

A suitable hydrometallurgical and environmentally friendly process was studied to replace the currently used practices for recycling lead-acid batteries via smelting. Metallic lead was recovered by cementation from industrial lead sludge solutions of urea acetate (200 to 500 g/L) using different types of metallic iron substrates (nails, shaving or powder) as reducing agents. Under specific operating conditions, up to 99.7% of lead acid battery paste, mainly composed of PbSO_4 , PbO_2 and PbO-PbSO_4 species, was converted to metallic lead. The conversion of the metallic lead and rate of the cementation reaction were strictly dependent on the type of iron substrate used as the reductant and the best operating conditions were found with iron powder. The rate constant of the lead recovery reaction under these conditions was $3 \cdot 10^{-3} \text{ s}^{-1}$ and the rate determining process was the diffusion controlled cathodic reaction ($E_a = 1.9 \text{ kJ/mol}$). The reaction residues and the recovered lead were characterized by XRD analysis. Metallic lead morphology and purity were studied by SEM and EDS respectively. Addition of proper amounts of concentrated sulphuric acid to the exhausted cementation solution led to the quantitative recovery of iron(II) by crystallization of $(\text{NH}_4)_2\text{SO}_4\text{FeSO}_4\cdot 6\text{H}_2\text{O}$.

© 2008 Elsevier B.V. All rights reserved.

1. Introduction

Since the adoption of the Basel Convention by more than eighty countries, the lead industry has been faced with a significant constriction of its potential future market (Helmer, 1996). In an effort to address the concerns of the regulators and communities that its products will be dealt with in ways that offer the highest level of safety, the lead industry started to develop the *green lead vision* which emphasizes the need to follow sustainable practices in the lead-acid battery industry (Roche and Toyne, 2004). The growth in the demand of lead-acid batteries, due to the increase in the number of automotive vehicles together with the more and stricter environmental regulations, created the need to relocate, modernize and reconvert processes for both batteries production and lead recycling in order to minimize their impact on the environment. Currently, lead recovery from exhausted lead-acid batteries is carried out by a pyrometallurgical route, causing environmental problems due to the emission in the atmosphere of lead particulates and sulphur dioxide (Valdez, 1997). Due to the increasingly stringent legislations for these emissions, there has been a large research effort to find a hydrometallurgical route to replace lead-acid battery recycling operations (Helmer, 1996). In particular, the electro-hydrometallurgical metal lead recovery route has been extensively studied and several pilot plants have been proposed. Lead electrowinning techniques, either in acidic or in

alkaline media, still do not overcome numerous technological problems nor avoid the parasitic formation of lead dioxide on the anode (Ferracin et al., 2002; Schwartz and Etsell, 1998; Gong et al., 1992a,b; Angelidis et al., 1985, 1989; Prengman, 1995; Ku and Lee, 1993; Sahoo and Rath, 1988; Chen and Dutrizac, 1996; Power and Ritche, 1975; Makhloufi et al., 1992).

The high PbO_2 content in the sludge represents the major problem in the leaching process. While PbO is readily dissolved by most of the leaching electrolytes, PbO_2 requires reduction of Pb(IV) to Pb(II) prior to leaching. Ferracin and his collaborators were able to solubilise completely samples of the sludge by using ascorbic acid solutions but the formation of an undesirable solid residue was observed after 24 h. (Ferracin et al., 2002)

Lead recovery using exhausted lead-acid battery paste with high content of metallic lead and antimony (approximately 13%) was reported by Maja et al. (1990). The high content of these metals was responsible of the reduction of most of Pb(IV) to Pb(II) species. The use of less noble metals for the hydrometallurgical recovery of heavy metals by cementation has also been investigated (Power and Ritche, 1975; Makhloufi et al., 1992). The recovery of lead from PbSO_4 using ammoniacal ammonium sulphate solution was studied by means of nickel powder as reductant. By this method, up to 90% of lead was recovered at 100°C after 3 h of reaction, but the metallic nickel was needed to be recovered by subsequent hydrogen reduction (Schwartz and Etsell, 1998). The cementation of lead onto rotating iron discs was shown to be a diffusion-controlled first-order reaction, with an activation energy of 9.6 kJ/mol (Makhloufi et al., 2000).

* Corresponding author. Tel.: +39 0916567232; fax: +39 0916567280.

E-mail address: volpe@dicpm.unipa.it (M. Volpe).

Table 1
Chemical composition of ESI S.p.A. industrial sludge from exhausted lead-acid batteries

Compound	Sludge composition (%w/w)
PbSO ₄	53.70
PbO	13.40
PbO ₂	22.40
CaSO ₄	8.50
Unidentified	2.00

Table 2
Chemical composition of synthetic sludge

Compound	Synthetic sludge composition (%w/w)
PbSO ₄	60.00
PbO	14.97
PbO ₂	25.03

In this study, we propose a new and industrially feasible hydrometallurgical process to recover metallic lead from lead-acid battery paste by cementation on iron, with observed efficiencies of up to 99.7%. The best operating conditions for lead-acid paste solubilisation using urea acetate solution and metallic lead cementation on soft steel nails or shavings or powder are reported, and the morphology of the deposited metal lead was investigated by SEM technique.

2. Experimental

2.1. Reactants and treatments of the lead-acid paste

Analytical grade lead compounds PbSO₄ (Carlo Erba RPE, 99%), PbO and PbO₂ (Sigma Aldrich A.C.S. reagent, +99%), were used in preliminary investigations in order to determine the best operating conditions for lead sludge solubilisation. Urea was purchased from Carlo Erba, glacial acetic acid was R.P. Normapure 100% and sulphuric acid was Carlo Erba RPE 96%. Samples of industrial lead-acid battery paste were provided by Ecological Scrap Industry S.p.A. (E.S.I., Pace del Mela, Messina, Italy). In Table 1, the average composition of the industrial sludge (E.S.I. sludge) is reported. Before any use, the sludge was finely disseminated and deprived of its moisture (about 12% w/w) by drying in an oven at 105 °C for at least 4 h. The high content of CaSO₄ in the acid battery paste was due to the addition of CaCO₃ to neutralize the excess of sulphuric acid coming from the battery crushing operation unit.

In order to gain a better knowledge of the mechanism of the solubility and cementation of the lead species, a synthetic lead-acid paste was prepared in our laboratory by mixing analytical grade lead compounds. Table 2 lists the percentage of the composition of the lead species, as commonly found in the industrial sludge.

2.1.1. Reducing substrates characteristics

Fig. 1 shows the three different types of soft steel substrates used in this work as reducing agents. U-shaped nails as commercially available

Table 3
Chemical composition of reducing substrates (iron at balance)

Substrate	C (%w/w)	Si (%w/w)	Mn (%w/w)
Nail	0.2	0.5	0.8
Shaving	0.2	0.4	1.0
Powder	0.2	0.5	0.5

Table 4
Reagent charges and operating conditions for cementation of lead using E.S.I. industrial sludge

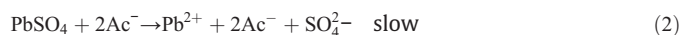
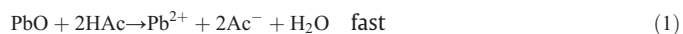
Reagent	Amount charged	Operating conditions
ESI sludge	50 g L ⁻¹ (Pb: 0.165 mol/L)	Temperature: 105 °C
Urea	500 g L ⁻¹ (8.326 mol/L)	Reaction time: 4 h
HAc	450 g L ⁻¹ (7.493 mol/L)	Agitation: 400 rpm
Fe ^c	50 g L ⁻¹ (0.895 mol/L)	Nitrogen atmosphere

(24 mm long, 12 mm wide and 2 mm thick) are shown in Fig. 1 a; shavings from industry scrap (approximately: 6 mm long, 6 mm wide and 0.5 mm thick) are shown in Fig. 1 b and soft steel powder obtained from Prometon is shown in Fig. 1 c. Table 3 lists the percentage of carbon, manganese and silicon elements (iron at balance) contained in the three reducing substrates. Morphology characteristics are reported and discussed in the results section.

2.2. Solubility tests

The study of solubility of analytical grade PbSO₄ and synthetic sludge in urea acetate solution was carried out in order to determine the best operating conditions for the solubilisation and cementation of the lead compounds when the E.S.I. industrial sludge was used as starting material. Previous studies carried out in our laboratory showed that the use of urea acetate solution represents the best compromise of solubility of lead(II) species compounds and pH of reaction solution maintaining a proper water / acetic acid ratio. The pH of solution should be as low as possible to avoid the separation of low soluble iron hydroxides during cementation reaction but not lower than pH 3 to maintain a suitable concentration of free acetate ions in solution.

In the presence of excess acetates lead monoxide is extremely more reactive than the lead sulphate, thus PbO is promptly converted to Pb(Ac)₂ in the presence of acetates:



Urea acetate solution was prepared by dissolving urea in H₂O/HAc solutions. The operating conditions investigated varied from 200 to 500 g/L of urea, H₂O/HAc ratio from 0.25 to 3.50 v/v, temperature from 70 to 105 °C and time of reaction from 1 to 4 h. For example, in order to

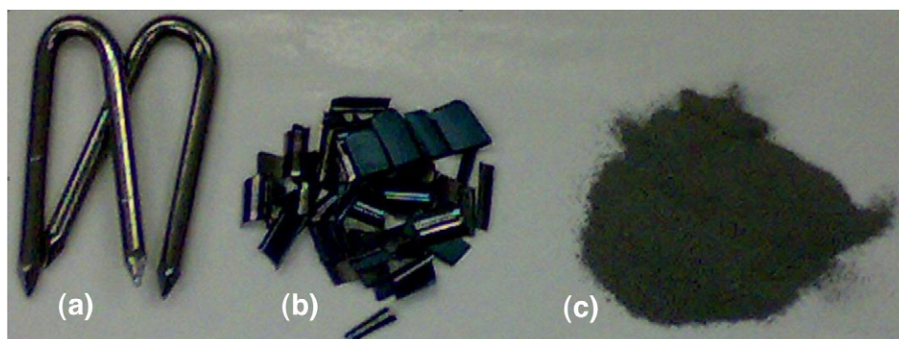


Fig. 1. Reducing agents substrates: a) nails, b) shavings, c) powder.

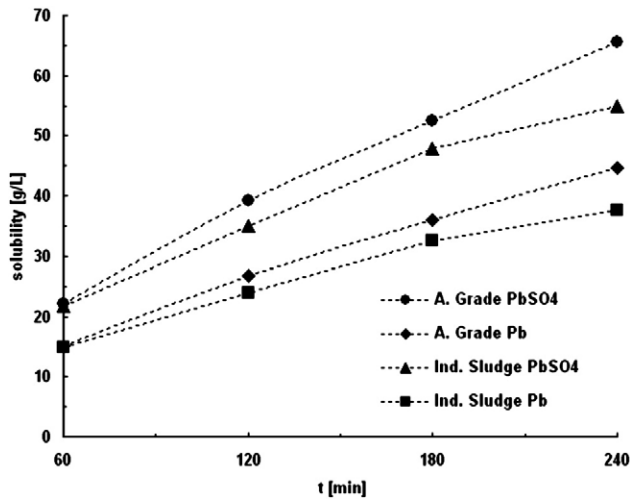


Fig. 2. Solubility comparison of analytical grade lead sulphate and lead sulphate contained in the industrial sludge as a function time.

prepare 0.25 L of 500 g/L solution of urea acetate (H_2O/HAc ratio 2.7 v/v), 125 g of urea were slowly dissolved, at room temperature, in a solution containing 116.5 mL of water and 43 mL of glacial acetic acid. The urea/acetate (w/w) ratio was approximately 2.8, the solution density 1.15 kg/L and pH=3.4.

During leaching, the lead ion concentration in solution was determined by atomic absorption analysis of solution samples drawn every hour throughout the course of the reaction. Insoluble PbO_2 or any unreacted $PbSO_4$ were collected by filtration, thoroughly rinsed with water, and dried in the oven prior to gravimetric determination.

2.3. Lead cementation procedures

The recovery of lead from $PbSO_4$, coming either from synthetic sludge or from E.S.I. industrial sludge was carried out by employing either a single step, or a two step procedure. In the former, all reactants were charged into the reactor simultaneously, whilst in the latter, the reducing agent was added after solubilisation of the lead compounds (Table 4). All the reaction steps were carried out under pure nitrogen atmosphere by using standard nitrogen-vacuum technique to avoid the oxidation of Fe(II) to Fe(III) (with the consequent precipitation of low soluble Fe(III) species) during the cementation reaction. The reaction system was realised by linking a vacuum/nitrogen line to a double necked 250 mL Pyrex round bottom flask fitted with a condenser to

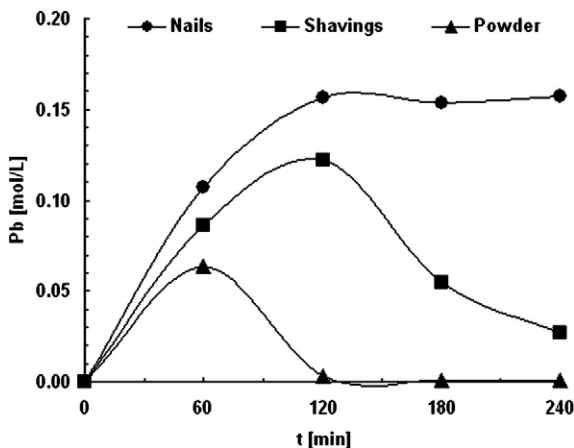


Fig. 3. Lead ions concentration variation during the course of the cementation reaction when soft steel nails, shavings or powder were used as reducing agents.

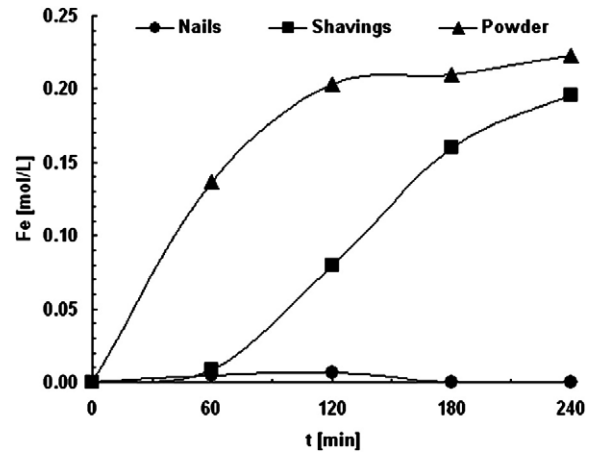


Fig. 4. Lead ions concentration variation during the course of the cementation reaction when soft steel nails, shavings or powder were used as reducing agents.

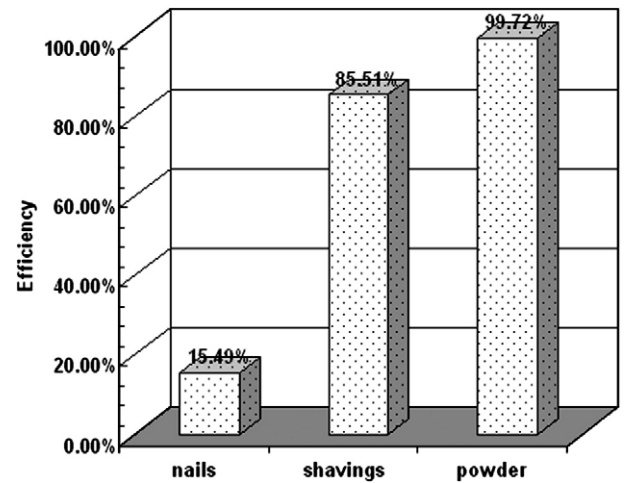


Fig. 5. Lead cementation efficiency, after 4 h of reaction, using different reducing substrates: nails, shavings, powder.

condense escaping vapors. During reaction, while nitrogen was left flowing continuously, the solution was stirred by a magnetic bar to approximately 400 rpm and heated up to the set point temperature in an ethylene glycol bath. Before adding the reactants, the urea/acetate solution was accurately deaerated and saturated with nitrogen.

In the single step procedure, the lead compounds and iron were added simultaneously into the reactor and the reaction progress was monitored every hour by atomic absorption spectroscopy analysis of the solution samples. The cemented lead, together with the unreacted iron, were collected, rinsed with distilled water and dried. The filtrate, held under inert atmosphere, was recovered for the successive sulphating reaction.

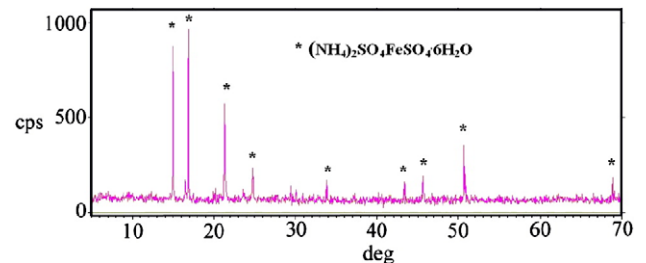


Fig. 6. XRD spectrum of iron(II) ammonium sulphate $(NH_4)_2SO_4FeSO_4 \cdot 6H_2O$.

Table 5
Ammonium ion concentrations for acidic hydrolysis of 500 g/L urea (acetate) solution

Time (h)	NH ₄ ⁺ (ppm) 25 °C	NH ₄ ⁺ (ppm) 105 °C
1	1.1	20.6
2	1.2	28.7

The two-step procedure is very similar to the single step one except that the reducing agent was added only after completion of the solubilisation step in order to evaluate the rate of the cementation reaction when different types of reducing substrates were used.

2.4. Sulphating procedure and residue crystallization

The addition of sulphuric acid to the filtrate solution enhanced the recovery of the low soluble iron(II) sulphate species. Sulphating reaction conditions were studied to attempt the formation of marketable pure heptahydrate species FeSO₄·7H₂O to recover the costs of metallic iron supply. The sulphating reaction was conducted at 105 °C by a two step process under inert atmosphere. Each step involved the addition of 10 mL of concentrated sulphuric acid followed by crystallization. Crystallization was conducted by first cooling the solution to room temperature followed by cooling the solution down to 0 °C using an ice bath.

3. Results and discussion

3.1. Solubility tests

The solubility of the analytical grade lead sulphate, as a function of time, was compared to the solubility of the lead sulphate species contained in the E.S.I. industrial sludge (Fig. 2). The best operating conditions were: 100 mL of urea acetate solution H₂O/HAc (v/v)=2.7, 500 g/L of urea, 4 h of reaction at 105 °C under nitrogen atmosphere. Analytical grade PbSO₄ gave a solubility up to 65.5 g/L after 4 h, corresponding to 44.7 g/L of Pb²⁺ in solution. On the other hand, when the industrial sludge was used under the same operating conditions, the equivalent PbSO₄ solubility was not higher than 55.0 g/L, corresponding to about 37.5 g/L of Pb²⁺ in solution.

3.2. Cementation reaction

The same operating conditions used for the solubilisation procedure were employed in the single step cementation reaction. Specifically, 5.6 g of ESI lead sludge containing 0.0185 mol of lead, and 6.0 g of iron, equivalent to 0.108 mol, were charged into the reactor flask containing 100 mL of a pre-heated urea acetate solution. Fig. 3 shows the variation of the Pb²⁺ concentration over time of reaction when the three different types of reductants were employed. During the cementation reaction, two opposite processes contributed to the Pb²⁺ concentration in solution: the first one is the solubilisation of the lead species contained in the sludge and the second one is the reduction of the Pb²⁺ coupled to the oxidation of Fe⁰ to form Pb⁰. As soon as Fe²⁺ was formed into the reaction system, it reacted with the undissolved PbO₂ forming Pb²⁺ and Fe³⁺ acetate species. The latter reacted with the excess Fe⁰ to give Fe²⁺ species. The operative conditions used in this study were properly set in order to avoid any precipitation of low solubility Fe(III) species.



Standard redox potential of the processes taking place during cementation are shown in Eqs. (8)–(10).



It was observed that during the first hour of reaction, the concentration of lead ions in solution increased in all the three cases. We conclude that, independently of the iron substrate used, the rate of the solubilisation process is higher than the reduction reaction. On the other hand, after

2.5. Characterization methods

The recovered lead and the reaction residues were characterized by XRD, SEM, and EDS analysis. The XRD patterns were obtained using a Philips (mod. PW 1130) generator and a Philips (mod. PW 1050) goniometer. The copper K α radiation and a scanning rate of 2 θ /min were used. Measured d spacings were compared with the ASTM index values. Morphology of the samples was examined at different magnifications using a FEI (mod. XL30 ESEM) scanning electron microscope. The presence of lead on the iron surface, used as reductant, was determined by FEI (mod. PV 9830/10E) EDS microprobe. The EDS analytical results were corrected for atomic number, absorbance and fluorescence (ZAF correction). The amount of lead(II) reacted, and iron(II) ions formed during the cementation reaction was evaluated by atomic absorption spectroscopy (AAS) using a Shimadzu AA6300 spectrophotometer. Specific surface area (SSA) values of iron shavings and powder were calculated by the BET equation in the interval $0.05 \leq (p/p^0) \leq 0.33$. Nitrogen physi-sorption experiments were performed at the liquid nitrogen temperature using a Micrometrics ASAP 2010 system. All the samples were degassed below 1.3 Pa at 250 °C prior to the measurements. Specific superficial areas of iron nails were evaluated considering a perfectly smooth surface.

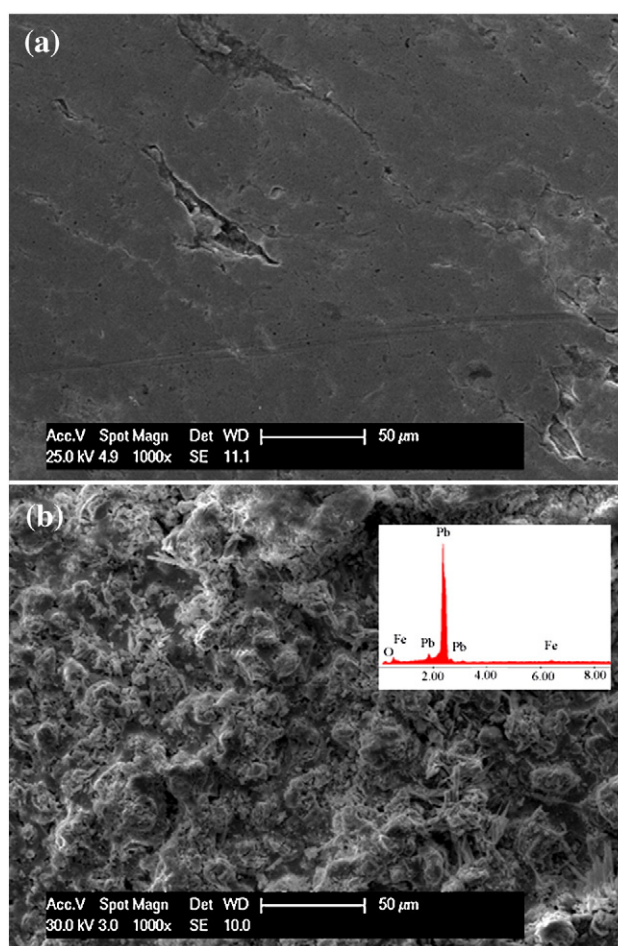
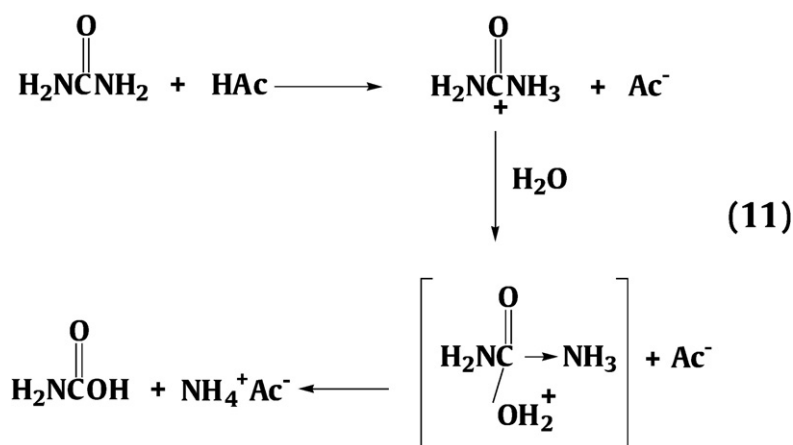


Fig. 7. SEM image of the iron nail surface prior to (a) and after (b) lead cementation reaction.

the first hour of reaction the concentration of lead ions in solution varied differently, dependent on the morphology and surface area of the reducing agent. In the case of soft steel nails, the concentration of the lead continued to increase until the second hour of reaction, reaching an approximately constant value of 0.16 mol/L. When soft steel shavings were used, the concentration rose to a maximum of 0.12 mol/L during the second hour of reaction then decayed to a value of 0.03 mol/L after 4 h. For the experiments that used soft steel powder as the reductant, the maximum was reached after just 1 h of reaction, then the Pb^{2+} concentration decreased down to zero after 2 h.

Analogously, Fig. 4 shows the variation of concentration of iron(II) over reaction time, as a function of the three different types of iron reductants used. It can be readily seen that when soft steel powder was employed, the concentration of Fe^{2+} rose fast due to the prompt oxidation reaction of metallic iron to Fe^{2+} by Pb^{2+} . On the other hand, when nails were used, the concentration of the iron(II) was very low; most likely due to the formation of a thin adherent layer of metallic lead over the nail that inhibited further diffusion of lead ions and oxidation of metallic iron. Fig. 5 shows the efficiency of the cementation after 4 h of reaction for the three different types of iron used, as



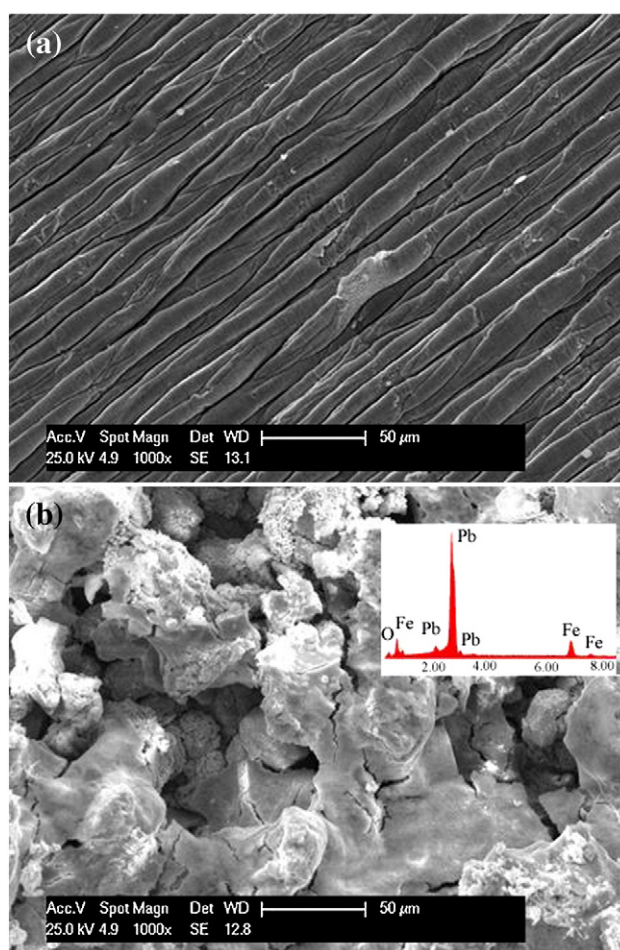


Fig. 8. SEM image of the iron shaving surface prior to (a) and after (b) lead cementation.

evaluated by the ratio of the metallic lead recovered to the total lead content. It was observed that efficiencies up to 99.7% were achieved when soft steel powder was used.

3.3. Sulphating reaction

The sulphating reaction was carried out to recover the iron(II) contained in the exhausted cementation solution. Crystallization of the sulphating solution led to the formation of a crop of pale green crystals. A detailed examination of the XRD spectrum reported in Fig. 6, together with the AA analysis of the crystals, suggested that the mixed ammonium sulphate species, $(\text{NH}_4)_2\text{SO}_4\text{FeSO}_4 \cdot 6\text{H}_2\text{O}$ was the predominant species formed. Only small traces of the desired $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ compound were detected. The formation of a stable mixed ammonium sulphate iron(II) species could be explained by the formation of NH_4^+ ions due to the acidic hydrolysis of urea under hot temperature.

In order to demonstrate this hypothesis, a 100 mL sample of urea acetate solution was heated to 105 °C for 2 h and the corresponding concentration of NH_4^+ ion was evaluated by ionic chromatography analysis. In Table 5, we report the concentration of NH_4^+ over time of reaction. The results show that the concentration of NH_4^+ ions in solution was particularly dependent on the reaction temperature. At 105 °C the concentration of NH_4^+ in the urea acetate solution after 2 h was 28.6 ppm — about twenty times higher than the concentration detected at room temperature.

3.4. Morphology characterization of iron substrates and recovered lead

Figs. 7–9 show SEM micrographs of iron nails, iron shavings and iron powder surfaces respectively before (a) and after (b) 4 h of lead cementation. The smooth nail surface before the reaction (Fig. 7 a) appears to be covered by a dense lead layer after completion of the cementation reaction (Fig. 7 b). This compact lead layer is probably responsible for prematurely blocking the reduction of Pb^{2+} to Pb^0 , thus inhibiting the cementation reaction. This is different to the results of the experiments when iron shavings were used, where the surface (Fig. 8 a) appears to be sensibly rougher than the nail surface. Fig. 8 b shows the surface of the iron shavings after 4 h of cementation reaction. The lead layer deposited on the surface is porous, thus leaving the iron metal surface exposed for further oxidation, although obviously, the rate of deposition lowered over time. Fig. 9 a shows the morphology of iron powder surface before the lead cementation reaction. The iron powder was observed to be covered by the metal lead deposit as soon as reaction starts consisting of spongy pellets of iron and lead aggregates a few millimetres in diameter. Fig. 9 b shows a micrograph of a section of an iron-lead pellet demonstrating the porosity of the pellets. The reaction solution is trapped in the sponge-like nature of the aggregates, thus allowing the lead cementation reaction to go to completion. Fig. 10 shows the XRD spectrum of finely disseminated sample of the aggregates after 4 h of reaction; it appears that only few traces of iron are detected in the sample.

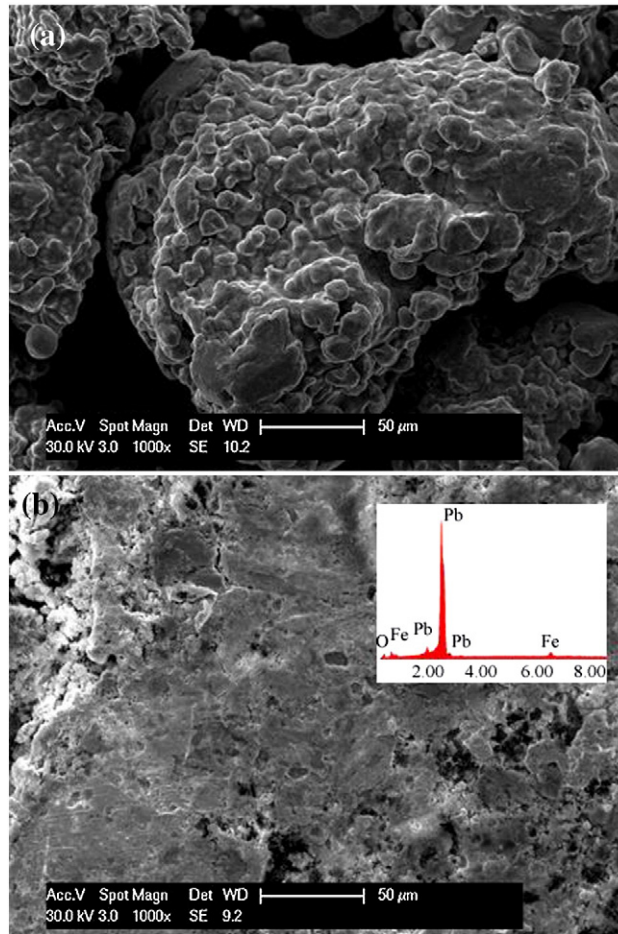


Fig. 9. SEM images of the iron powder surface prior to (a) and after (b) lead cementation.

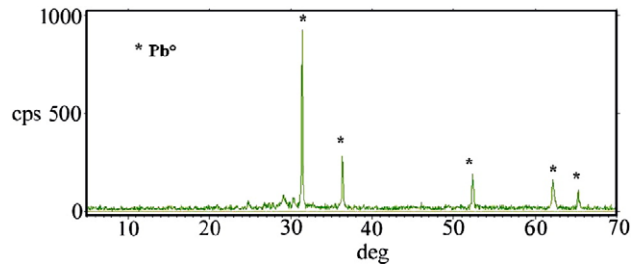


Fig. 10. XRD spectrum of lead metal deposited over the reducing substrate.

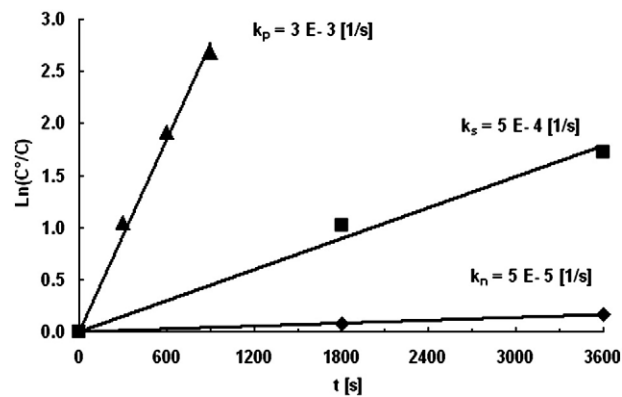


Fig. 11. Kinetic plots of the cementation reaction for the different reducing substrates: ▲ powder; ■ shavings; ◆ nails.

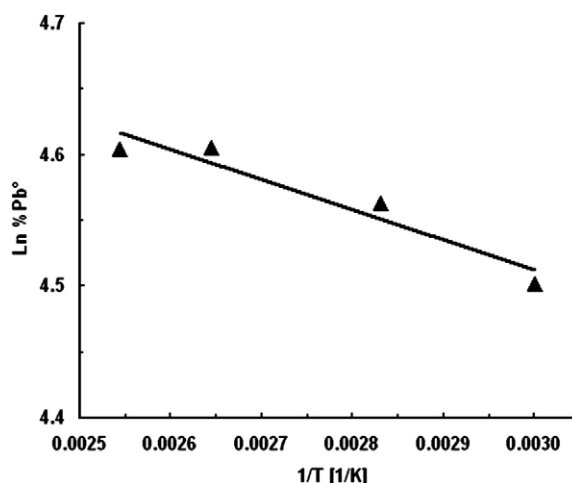


Fig. 12. Arrhenius Plot of the cementation reaction, when soft steel powder was used as reducing agent.

3.5. Kinetics of the lead cementation reaction over iron

The kinetics of the lead cementation reaction for the formation of Pb^{2+} was studied by monitoring Pb^{2+} concentration changes over time in the urea acetate solution (pH=3.40). For this study, we used the two-step procedure that was described earlier. Analytical grade PbSO_4 ($18.3 \cdot 10^{-3}$ mol) was added to 100 mL of 500 g/L of urea acetate solution; the solution was warmed up to 105 °C with stirring at 400 rpm. As soon as the lead(II) species were dissolved, 6.0 g of iron were charged to the reaction flask to carry out the cementation reaction.

In Fig. 11, the plots of $\ln(C^\circ/C)$ vs. time show the reaction to be first-order and the kinetic law could be written as follows.

$$\ln(C^\circ/C) = (A_c K_{pb}/V)t = kt \quad (12)$$

where A_c is the cathodic area, V the volume of solution, K_{pb} the mass transfer coefficient and k the first order kinetic constant. The kinetic constants for lead cementation were determined by evaluating the slopes of the $\ln(C^\circ/C)$ plots over time, and were measured for each of the three different iron substrates. The kinetic constant values were: $k_p = 3.1 \cdot 10^{-3}$ 1/s for iron powder, $k_s = 5 \cdot 10^{-4}$ 1/s for iron shaving and $k_n = 5 \cdot 10^{-5}$ 1/s for iron nails respectively. Therefore, the rate of cementation reaction using iron powder was 6.2 times higher than the rate of cementation using iron shavings. This result was explained by the BET experiment which showed that the ratio of the specific surface area of iron powder ($A_p = 0.19 \text{ m}^2/\text{g}$) to the iron shavings ($A_s = 0.03 \text{ m}^2/\text{g}$) was equal to 6.4, very close to the ratio of their reaction rates. Fig. 12 shows the Arrhenius plot for the cementation reaction when iron powder was used as reducing agent. The activation energy E_a , estimated by Arrhenius law, was 1.9 kJ/mol, which is also in good agreement with a first-order reaction that is controlled by a diffusion process in solution (Makhloufi et al., 2000).

4. Conclusions

In this work, a new, environmentally friendly route to replace the traditional lead-acid battery smelter recycling operation is proposed. The recovery of metallic lead, up to 99.7%, of the lead content of the industrial lead-acid battery paste was achieved by a lead cementation reaction using urea acetate solution as a leaching agent and iron as the reductant. The reaction rate was found to be strictly dependent on the specific surface area of the iron reducing substrate. The cementation reaction was found to be the step controlling the rate of the process, with a first order kinetic behaviour controlled by diffusion.

A hydrometallurgical urea/acetate plant for the recovery of metallic lead from the exhausted lead acid battery paste presents several technological challenges compared to the traditional pyrometallurgical rotary kilns. The most evident complication being the need of three units: a reactor, filter and crystallizer kept at the solution boiling temperature over a positive pressure of nitrogen. On the other hand several advantages make it very desirable: such as the absence of SO_2 , SO_3 , NO_x gas emission and lead containing particulate matter; lower energy consumption; higher quantity of metal lead recovered for unit of mass of sludge, (higher efficiency); lower costs of operation, considering the high costs of energy supply, toxic gas treatments and the discharge of the lead containing oven slag.

Preliminary studies conducted in our laboratories show that urea solution can be efficiently recovered and recycled to the cementation reactor thus limiting the discharge and treatment of environmentally hazardous nitrogen compounds.

5. List of symbols

Symbol	Meaning
A_c	Cathodic area (m^2)
A_n	Specific surface area of the nail (m^2/g)
A_p	Specific surface area of the powder (m^2/g)
A_s	Specific surface area of the shaving (m^2/g)
C	Actual concentration of Pb^{2+} in solution (mol/L)
C°	Initial concentration of Pb^{2+} in solution (mol/L)
E_a	Activation energy (KJ/mol)
k_n	Kinetic constant, nail, (1/s)
k_p	Kinetic constant, powder, (1/s)
k_s	Kinetic constant, shaving, (1/s)
K_{pb}	Mass transfer coefficient, (m/s)
t	Time of reaction (s)
V	Volume of reaction solution (m^3)

Acknowledgements

We gratefully acknowledge E.S.I. S.p.A. for the financial support.

References

- Angelidis, T., Fytianos, K., Vasilikiotis, G., 1985. Kinetic study of lead cementation by iron powder in wastewater. *Chemosphere* 14 (8), 1001–1012.
- Angelidis, T., Fytianos, K., Vasilikiotis, G., 1989. Lead recovery from aqueous solution and waste by cementation utilizing an iron rotating disc. *Resources, Conservation and Recycling* 2 (2), 131–138.
- Chen, T.T., Dutrizac, J.E., 1996. The mineralogical characterization of lead acid battery paste. *Hydrometallurgy* 40, 223–245.
- Ferracin, L.C., Chàcon-Sanhueza, A.E., Davoglio, R.A., Rocha, L.O., Caffeu, D.J., Fontanetti, A.R., Rocha-Filho, R.C., Biaggio, S.R., 2002. Lead recovery from a typical Brazilian sludge of exhausted lead-acid batteries using an electrohydrometallurgical process. *Hydrometallurgy* 65, 137–144.
- Gong, Y., Dutrizac, J.E., Chen, T.T., 1992a. The conversion of lead sulphate to lead carbonate in sodium carbonate media. *Hydrometallurgy* 28, 399–421.
- Gong, Y., Dutrizac, J.E., Chen, T.T., 1992b. The reaction of anglesite (PbSO_4) with sodium carbonate solutions. *Hydrometallurgy* 31, 175–199.
- Helmer, J.W., 1996. The Basel convention: effect on the Asian secondary lead industry. *Journal of Power Sources* 59, 1–7.
- Ku, Y., Lee, C.S., 1993. Kinetic study on the removal of lead from wastewaters by iron cementation. *Journal of the Chinese Institute of Engineers* 20 (3), 295–301.
- Maja, M., Penazzi, N., Baudino, M., Ginatta, M.V., 1990. Recycling of the lead-acid batteries: the Ginatta process. *Journal of Power Sources* 31, 287–294.
- Makhloufi, L., Bourouina, S., Haddad, S., 1992. Cèmentation électrochimique de l'argent par la cuivre en milieu concentré de chlorures. *Electrochimica Acta* 34, 1779–1786.
- Makhloufi, L., Saidani, B., Hammache, H., 2000. Removal of lead ions from acidic aqueous solutions by cementation on iron. *Water Resources* 34, 2517–2524.
- Power, G.P., Ritche, I.M., 1975. Modern aspect of electrochemistry. In: Conway, B.E., Bockris, J.O'M (Eds.), Plenum Press, New York.
- Prengman, R.D., 1995. Recovering lead from batteries. *JOM* 47 (1), 31–33.
- Roche, M., Toyne, P., 2004. Green lead-oxymoron or sustainable development for the lead-acid battery industry. *Journal of Power Sources* 133, 3–7.
- Sahoo, P.K., Rath, P.C., 1988. Recovery of lead from complex sulphide leach residue by cementation with iron. *Hydrometallurgy* 20 (Issue 2), 169–177.
- Schwartz, L.D., Etsell, T.H., 1998. The cementation of lead from ammoniacal ammonium sulphate solution. *Hydrometallurgy* 47, 273–279.
- Valdez, H., 1997. Lead battery markets and recycling in Mexico and South America. *Journal of Power Sources* 67, 219–223.